

Supporting Information for:

The oxidation of pyridines catalyzed by surfactant-encapsulated polyoxometalate of [(C₁₈H₃₇)₂(CH₃)₂N]₈[HBW₁₁O₃₉] with temperature-responsive property of solubility

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1. Experimental

1.1 Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

1.2 Characterization techniques

Infrared spectra were recorded on a Nicolet 170 FT-IR spectrometer using KBr pellets. Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (Vario EL Cube). XRD data were collected on a Bruker D8-advance with Cu-K α radiation. The TG analysis was performed on a Perkin-Elmer 7 thermal analysis instrument in flowing N₂ with a heating rate of 10K min⁻¹ from 25 to 1000°C. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE \square -400 MHz spectrometer with TMS as an internal standard and CDCl₃ as solvent.

2. IR spectrum of SEP-BW₁₁

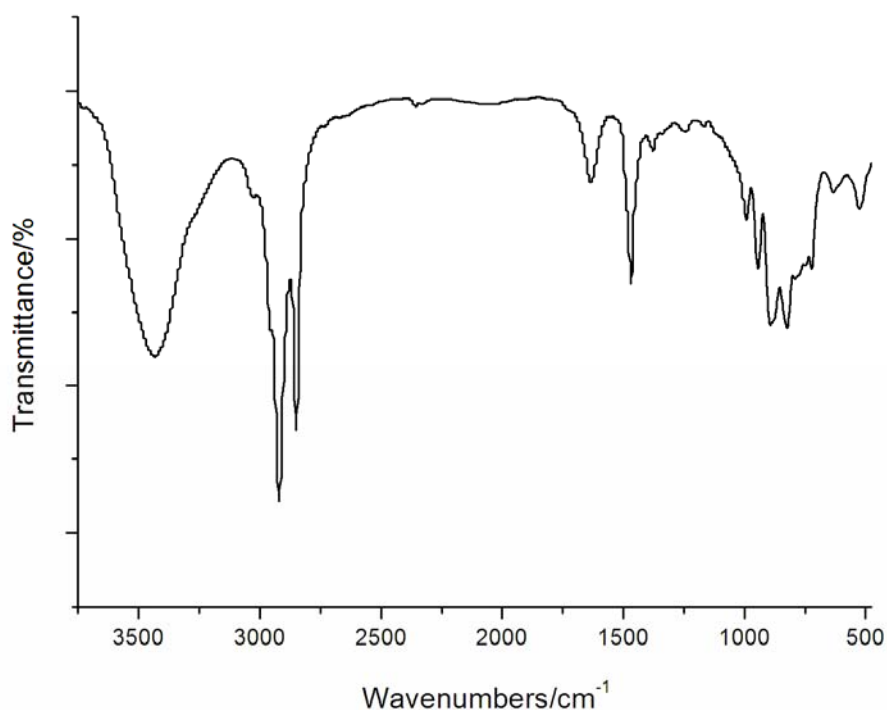


Fig. S1 IR spectrum of SEP-BW₁₁

3. ^1H NMR and ^{13}C NMR of SEP-BW₁₁

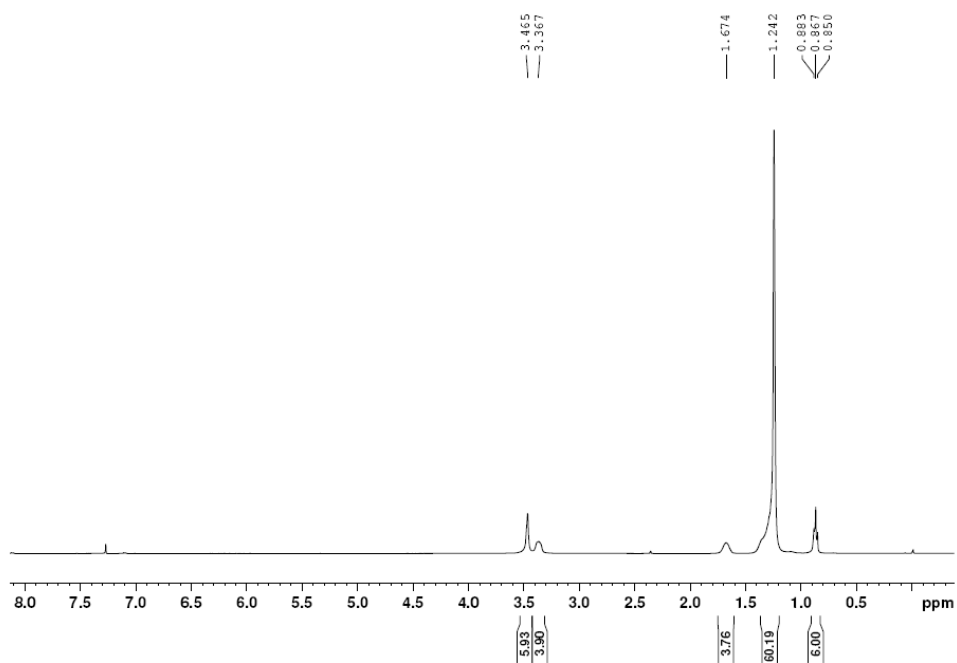


Fig. S2 ^1H NMR of SEP-BW₁₁

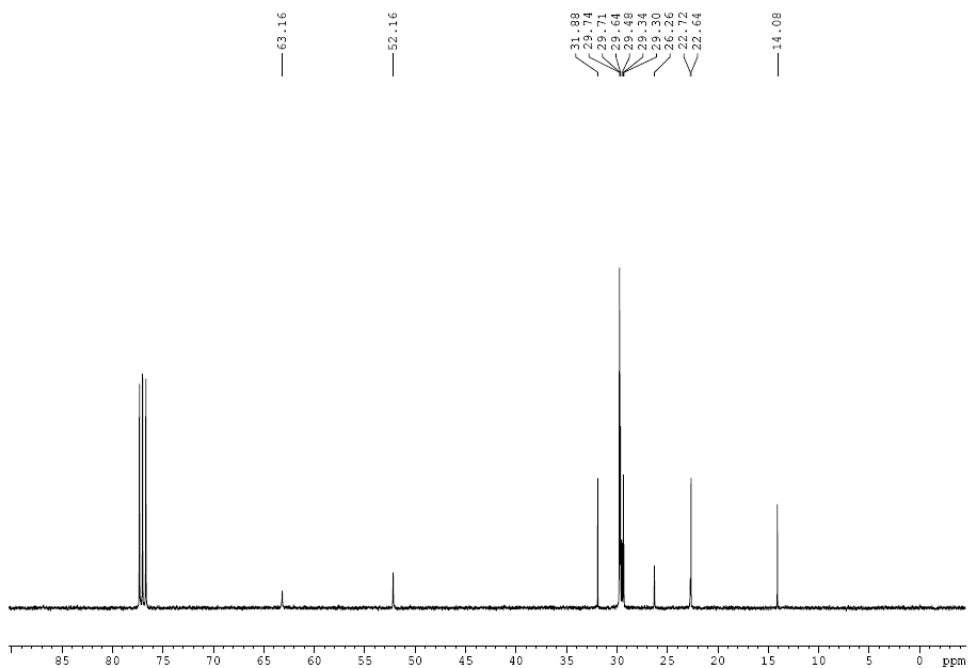


Fig. S3 ^{13}C NMR of SEP-BW₁₁

4. IR spectrum of the used catalyst

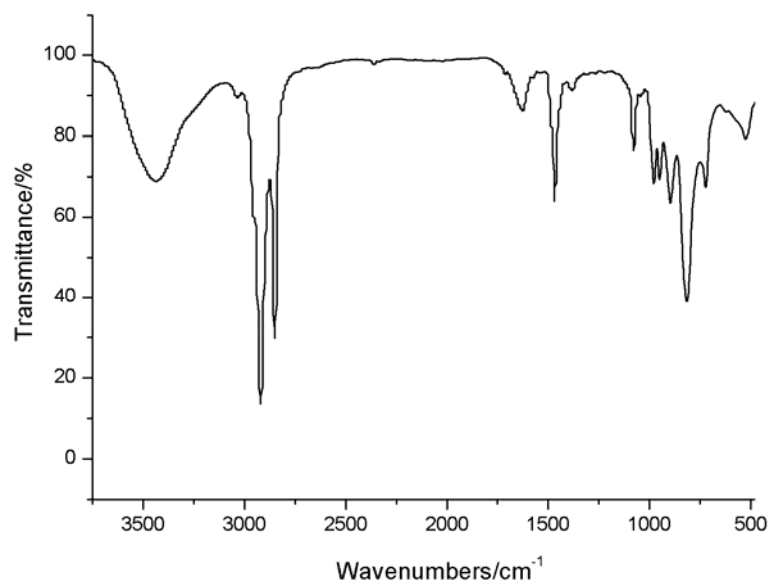


Fig. S4 IR spectrum of the used catalyst

5. ¹H NMR and ¹³C NMR of the used catalyst

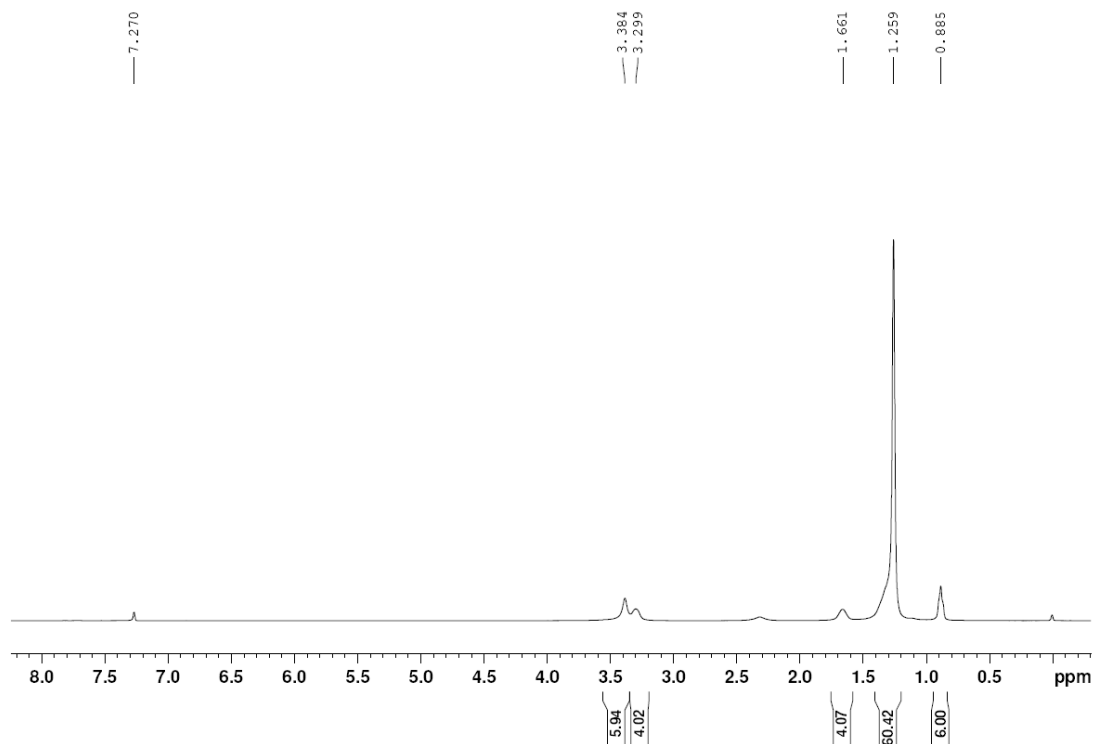


Fig. S5 ¹H NMR of the used catalyst

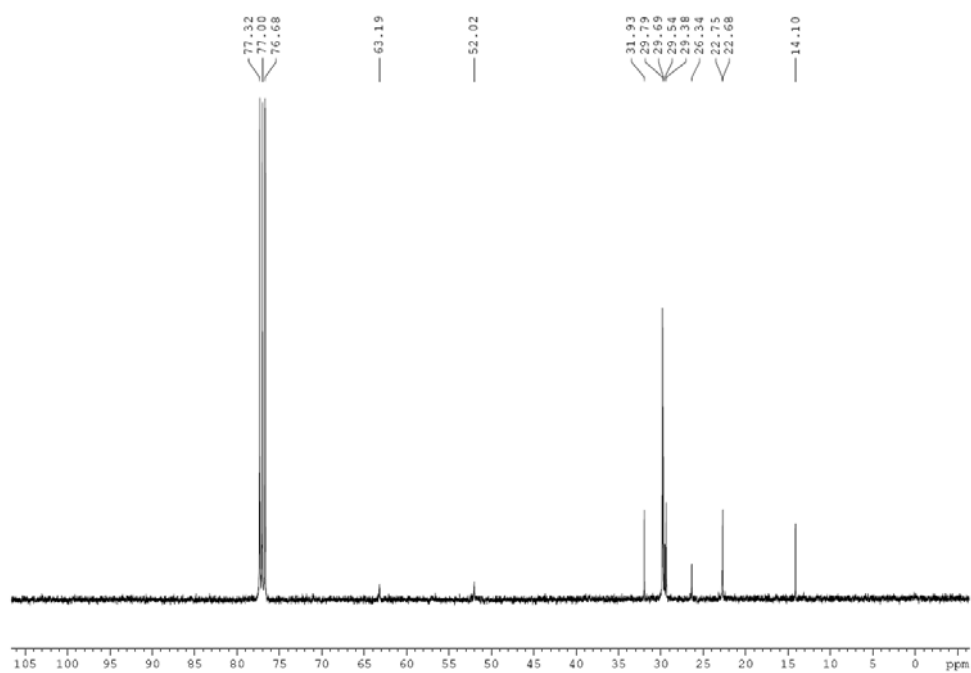


Fig. S6 ^{13}C NMR of the used catalyst

6. XRD pattern of SEP-BW₁₁

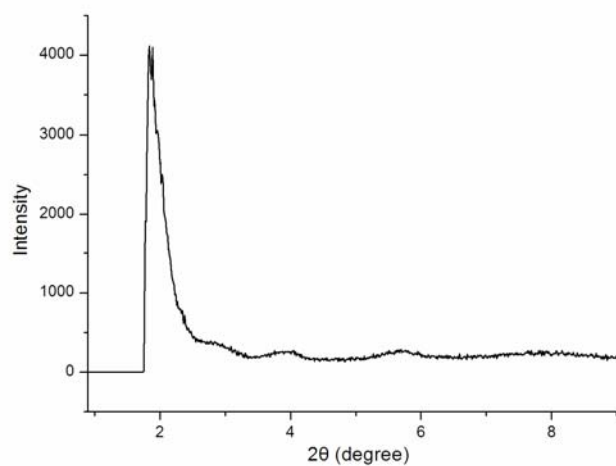


Fig. S7 Low-angle XRD pattern of SEP-BW₁₁

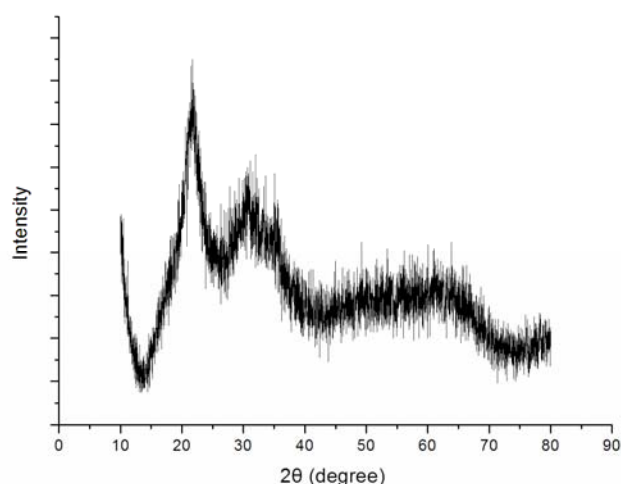


Fig. S8 Wide-angle XRD pattern of SEP-BW₁₁

7. Characterization of oxidation products ^[1-4]

Pyridine-N-oxide

¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.22-8.21 (d, J=4 Hz, 2 H), 7.44-7.41 (t, 2 H), 7.37-7.33 (t, 1 H); ¹³C NMR(DMSO-*d*₆, 400 MHz) δ 125.7 (2C), 126.9, 139.0 (2C).

2-Picoline-N-oxide

¹H NMR (CDCl₃, 400 MHz) δ 8.17-8.15 (d, J=8 Hz, 1 H), 7.18-7.16 (d, J=8 Hz, 1 H), 7.12-7.04 (m, 2 H), 2.41 (s, 3 H); ¹³C NMR(CDCl₃, 400 MHz) δ 17.6, 123.4, 125.6, 126.4, 139.1, 148.8.

2,3-Lutidine-N-oxide

¹H NMR (CDCl₃, 400 MHz) δ 8.24 (s, 1 H), 7.03-6.99 (t, 2H), 2.47 (s, 3H), 2.29 (s, 3H); ¹³C NMR(CDCl₃, 400 MHz) δ 13.8, 19.4, 121.9, 127.6, 134.8, 137.3, 148.4.

2,6-Lutidine-N-oxide

¹H NMR (CDCl₃, 400 MHz) δ 7.15-7.13 (d, J=8 Hz, 1 H), 7.10-7.06 (m, 2 H), 2.52 (s, 6 H); ¹³C NMR(CDCl₃, 400 MHz) δ 18.3 (2C), 124.0 (2C), 125.0, 149.0 (2C).

2-Chloropyridine-N-oxide

¹H NMR (CDCl₃, 400 MHz) δ 8.30 (d, 1 H), 7.47-7.45 (t, 1 H), 7.20-7.18 (t, 2 H); ¹³C NMR(CDCl₃, 400 MHz) δ 123.9, 126.0, 127.1, 140.5, 141.8.

Quinoline-N-oxide

¹H NMR (CDCl₃, 400 MHz) δ 8.74-8.72 (d, J=8 Hz, 1 H), 8.53-8.52 (d, J=4 Hz, 1 H), 7.87-7.85 (d,

J=8 Hz, 1 H), 7.75-7.73 (d, J=8 Hz, 2 H), 7.65-7.61 (t, 1 H), 7.29-7.27 (d, J=8 Hz, 1 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 119.7, 120.9, 126.1, 128.1, 128.7, 130.4 (2C), 135.6, 141.5.

Isoquinoline-N-oxide

^1H NMR (CDCl_3 , 400 MHz) δ 8.65 (s, 1 H), 8.00-7.99 (d, J=4 Hz, 1 H), 7.64-7.62 (d, J=8 Hz, 1 H), 7.58-7.52 (m, 2 H), 7.47-7.41 (m, 2 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 124.2, 125.0, 126.7, 128.8, 129.0, 129.5, 129.6, 136.2, 136.9.

4-Methyl-quinoline-N-oxide

^1H NMR (CDCl_3 , 400 MHz) δ 8.79-8.77 (d, J=8 Hz, 1 H), 8.45-8.44 (d, J=4 Hz, 1 H), 7.94-7.92 (d, J=8 Hz, 1 H), 7.73-7.71 (d, J=8 Hz, 1 H), 7.66-7.64 (d, J=8 Hz, 1 H), 7.09 (s, 1 H), 2.63 (s, 3 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 18.2, 120.3, 121.4, 124.6, 128.4, 129.8, 130.0, 134.6, 135.0, 140.9.

8-hydroxy-quinoline-N-oxide

^1H NMR (CDCl_3 , 400 MHz) δ 15.1 (s, 1 H), 8.23-8.20 (m, 1 H), 7.79-7.75 (m, 1 H), 7.49-7.43 (m, 1 H), 7.25-7.21 (m, 2 H), 7.05-7.00 (m, 1 H); ^{13}C NMR(CDCl_3 , 400 MHz) δ 114.7, 116.7, 120.3, 129.6, 129.7, 130.5, 132.1, 134.4, 153.8.

8. References

- [1] F. A. L. Anet and I. Yavari, *J. Org. Chem.*, 1976, **41**, 3589.
- [2] S. A. Sojka, F. J. Dinan and R. Kolarczyk, *J. Org. Chem.*, 1979, **44**, 307.
- [3] C. Copéret, H. Adolfsson, T.-A. V. Khuong, A. K. Yudin and K. B. Sharpless, *J. Org. Chem.*, 1998, **63**, 1740.
- [4] Y. Ding, W. Zhao, W. F. Song, Z. X. Zhang and B. C. Ma, *Green Chem.*, 2011, **13**, 1486.